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(54) **Polystyrene composition**

Polystyrol - Zusammensetzung

Composition de polystyrène

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(73) Proprietor: **IDEMITSU KOSAN COMPANY
LIMITED
Tokyo 100 (JP)**

(72) Inventor: **Okada, Akihiko
Ichihara-shi, Chiba-ken (JP)**

(74) Representative: **Türk, Gille, Hrabal, Leifert
Brucknerstrasse 20
40593 Düsseldorf (DE)**

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DescriptionBACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a novel polystyrene composition. More particularly, it pertains to a syndiotactic polystyrene composition which is greatly improved in impact resistance, elongation and retention of physical properties during recycling without detriment to heat resistance and modulus of elasticity.

2. Description of Related Arts

A styrenic polymer having syndiotactic configuration (SPS) is excellent in heat resistance and chemical resistance but is poor in impact resistance and therefore, it has heretofore suffered the disadvantage that it is inevitably limited in the scope of application as a construction material. In order to solve the above-mentioned problem, attempts have been made to improve the impact resistance of SPS, for example, by blending a rubbery elastomer and/or other thermoplastic resin with SPS. (Refer to Japanese Patent Application Laid-Open Nos. 257950/1987, 146944/1989, 182344/1989, 279944/1989 and 64140/1990.)

In particular, Japanese Patent Application Laid-Open No. 146944/1989 proposes the use of a styrenic compound as a component and as a rubbery elastomer and Japanese Patent Application Laid-Open No. 279944/1989 proposes the addition of block or graft copolymer containing atactic polystyrene chain as a compatibilizer to a SPS/rubber composition.

However, since there is used in the above-proposed composition, a rubbery component itself or a block or graft copolymer containing atactic polystyrene chain as a compatibilizer for the purpose of improving the compatibility between inherently incompatible SPS and the rubbery component and enhancing the dispersibility and interfacial strength of the rubbery component, the problem still remains unsolved in that the working effect as the compatibilizer is insufficient resulting in slight enhancement of impact resistance. On the other hand, the addition of a large amount of the rubbery component or the compatibilizer containing atactic polystyrene chain for the purpose of sufficiently enhancing the impact resistance brings about a problem that the heat resistance and modulus of elasticity of the resultant composition are inevitably lowered to a great extent.

SUMMARY OF THE INVENTION

The object of the present invention under such circumstances is to provide a polystyrene composition which is remarkably improved in its impact resistance and elongation without detriment to its heat resistance and modulus of elasticity and also well suited to be molded into industrial materials such as electric and electronic materials, industrial construction materials, car parts, domestic electrical appliances and various mechanical parts.

In view of the above, intensive research and investigation were continued by the present inventors in order to develop a polystyrene composition provided with the aforesaid favorable properties. As a result, it has been found by the present inventors that a syndiotactic polystyrene composition which is greatly improved in impact resistance, elongation and retention of physical properties during recycling without detriment to heat resistance and modulus of elasticity is obtained by preparing in advance a high molecular compound comprising a syndiotactic polystyrene (SPS) and a rubbery elastomer and then further blending it with SPS as the base material or by forming a high molecular compound comprising SPS and a rubbery elastomer while being blended with SPS as the base material; that the above-mentioned high molecular compound is usable as a compatibilizer between SPS and the rubbery elastomer, and also a syndiotactic polystyrene composition which is greatly improved in impact resistance, elongation and retention of physical properties during recycling without detriment to heat resistance and modulus of elasticity is obtained even by a small addition of such compatibilizer when the aforesaid composition is compared with the compound obtained by simply blending SPS with the rubbery elastomer; and that by compounding an inorganic filler with the foregoing impact-resistant syndiotactic polystyrene composition, there is obtained a resin composition which is increased in modulus of elasticity and heat distortion temperature and, as compared with as resin composition not compounded with the above-mentioned high molecular compound, is remarkably improved in impact strength and elongation. The present invention has been accomplished on the basis of the aforesaid finding and information.

Specifically, the first aspect of the present invention provides a polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of a styrenic polymer having syndiotactic configuration (a) and 100 to 1% by weight of a styrenic polymer having syndiotactic configuration and a functional group (b); and 1 to 100 parts by weight of a rubbery elastomer which can react with said functional group of the component (b) as the component (c), said components (a)+(b) and (c) being blended with each other, wherein the component (b) and the

component (c) are constituting a high molecular compound prepared by reaction. The second aspect thereof provides a polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of the component (a) and 100 to 1% by weight of the component (b); 1 to 10 parts by weight of the component (c); and 1 to 100 parts by weight of a rubbery elastomer (d), said components (a)+(b), (c) and (d) being blended with each other, wherein the component (b) and the component (c) are constituting a high molecular compound prepared by reaction. The third aspect thereof provides a polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of the component (a) and 100 to 1% by weight of the component (b); 1 to 100 parts by weight of the component (c); and 1 to 350 parts by weight of an inorganic filler (e), said components (a)+(b), (c) and (e) being blended with each other, wherein the component (b) and the component (c) are constituting a high molecular compound prepared by reaction. The fourth aspect thereof provides a polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of the component (a) and 100 to 1% by weight of the component (b); 1 to 10 parts by weight of the component (c); 1 to 100 parts by weight of the component (d); and 1 to 350 parts by weight of the component (e), said components (a)+(b), (c), (d) and (e) being blended with each other wherein the component (b) and the component (c) are constituting a high molecular compound prepared by reaction.

In the composition according to the present invention, there is used the resin component comprising 0 to 99% by weight of a styrenic polymer having syndiotactic configuration (a) and 100 to 1% by weight of a styrenic polymer having syndiotactic configuration and a functional group (b).

DESCRIPTION OF PREFERRED EMBODIMENT

Here, the styrenic polymer having syndiotactic configuration (a) means that its stereochemical structure is of syndiotactic configuration, i.e. the stereostructure in which phenyl groups of substituted phenyl groups as side chains are located alternately at opposite directions relative to the main chain consisting of carbon-carbon bonds. Tacticity is quantitatively determined by the nuclear magnetic resonance method (^{13}C -NMR method) using carbon isotope. The tacticity as determined by the ^{13}C -NMR method can be indicated in terms of proportions of structural units continuously connected to each other, i.e., a diad in which two structural units are connected to each other, a triad in which three structural units are connected to each other and a pentad in which five structural units are connected to each other. "The styrenic polymers having such syndiotactic configuration as mentioned in the present invention usually means polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(halogenated alkylstyrene), polypoly(alkoxystyrene), poly(vinyl benzoate), hydrogenated polymer thereof, the mixture thereof, and copolymers containing the above polymers as main components, having such a syndiotacticity as determined by the above-mentioned method that the proportion of racemic diad is at least 75%, preferably at least 85%, or the proportion of racemic pentad is at least 30%, preferably at least 50%. The poly(alkylstyrene) includes poly(methylstyrene), poly(ethylstyrene), poly(isopropylstyrene), poly(tert-butylstyrene), poly(phenylstyrene), poly(vinylnaphthalene) and poly(vinylstyrene). Poly(halogenated styrene) includes poly(chlorostyrene), poly(bromostyrene), and poly(fluorostyrene). Poly(halogenated alkylstyrene) includes poly(chloromethylstyrene). Poly(alkoxystyrene) includes poly(methoxystyrene), and poly(ethoxystyrene).

The particularly desirable styrenic polymers are polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), hydrogenated polystyrene and the copolymer containing the structural units thereof.

The molecular weight of the styrenic polymer to be used in the present invention is not specifically limited, but is desirably 10,000 or more, more desirably 50,000 or more in terms of weight-average molecular weight. The molecular-weight distribution, that is, the broadening of molecular weight of the styrenic polymer is not specifically limited as well, but may be in a wide range. A weight-average molecular weight of less than 10,000 is unfavorable since the composition or molding obtained is deteriorated thereby in the thermal and mechanical properties.

The styrenic polymer having such syndiotactic configuration can be produced by polymerizing a styrenic monomer which corresponds to the above styrenic polymer in the presence or absence of a solvent such as an inert hydrocarbon by the use of a catalyst comprising a titanium compound and a condensation product of water and trialkylaluminum (Japanese Patent Application Laid-Open No. 187708/1987). In addition, the poly(halogenated alkylstyrene) and the hydrogenated product thereof can be produced by the processes described in Japanese Patent Application Laid-Open Nos. 46912/1989 and 178505/1989, respectively.

On the other hand, the styrenic polymer having syndiotactic configuration and a functional group as the component (b) is a modified product from the above-mentioned styrenic polymer having syndiotactic configuration, and is produced by, for example, (1) introduction of a functional group through copolymerization at the time of polymerization, (2) introduction of a functional group at the time of cessation of polymerization or (3) grafting by taking advantage of the aforementioned item (1) of (2), any of which however, does not limit the production method thereto. In addition, the modification rate is not specifically limited.

Examples of the modified product through the item 1) include copolymer of styrene and p-methylstyrene or divi-

nylbenzene, those through the item 2) include glycidyl methacrylate-end-modified SPS and maleic anhydride-end-modified SPS and those through the items 3) include styrene/divinylbenzene copolymer onto which glycidyl methacrylate is grafted and styrene/p-methylstyrene copolymer onto which maleic anhydride is grafted in the presence of a radical generating agent.

In the composition according to the present invention there is used as the component (c), a rubbery elastomer which can react with the functional group of the styrenic polymer having syndiotactic configuration and a functional group as the component (b). Examples of such rubbery elastomer include natural rubber, polybutadiene, polyisoprene, polyisobutylene, neoprene, polysulfide rubber, thiokol rubber, acrylic rubber, urethane rubber, silicon rubber, epichlorohydrin rubber, styrene/butadiene block copolymer (SBR), styrene/butadiene/styrene block copolymer (SBS), hydrogenated styrene/butadiene/styrene block copolymer (SEBS), styrene/isoprene block/styrene block copolymer (SIS) hydrogenated styrene/isoprene block/styrene block copolymer (SEPS), ethylene/propylene rubber (EPR), ethylene/propylene/diene rubber (EPDM) and modified rubbers therefrom.

Among the above-mentioned elastomers, SEBS, SBR, SBS, SEPS, and SIS are preferably used in particular. Examples of the particularly desirable modified rubbers include maleic anhydride-modified SEBS, maleic anhydride-modified EPR, epoxy group-modified SEBS and rubber-modified EPR. In the second second and fourth aspects of the present invention, there is preferably used a rubbery elastomer in the component (c) which is the same as or compatible with the rubbery elastomer in the component (d). It is necessary in the first and third aspects of the present invention that 1 to 100 parts by weight of the rubbery elastomer as the component (c) be blended with 100 parts by weight of the SPS-based resin component comprising the components (a) and (b). An amount of the component (c) less than 1 part by weight results in failure to sufficiently exert the effect on improving impact resistance, whereas that more than 100 parts by weight will cause undesirable decrease in the modulus of elasticity and heat resistance of the composition due to the influence of the rubbery elastomer.

It is necessary in the second and forth aspects of the present invention that 0.1 to 10 parts by weight of the rubbery elastomer as the component (c) be blended with 100 parts by weight of the SPS-based resin component comprising the component (a) and (b). An amount of the component (c) less than 0.1 part by weight results in failure to sufficiently exhibit the effect as the compatibilizer, whereas that more than 10 parts by weight will cause unfavorable decrease in the modulus of elasticity and heat resistance of the composition and also disadvantage in the production cost of the composition.

It is important in the composition according to the present invention that the above-mentioned styrenic polymer having syndiotactic configuration and a functional group (modified SPS) as the component (b) and the rubbery elastomer as the component (c) constitute a high molecular compound, which can be prepared by the reaction (1) among modified SPS/rubbery elastomer/crosslinking agent, (2) among modified SPS/modified rubber/crosslinking agent or (3) between modified SPS/modified rubber.

The above-mentioned high molecular compound is obtained by reacting with a crosslinking agent in the presence or absence of a solvent and an other type of resin or by reacting the functional groups of a modified polymer directly or by the use of a crosslinking agent. The reaction is effected by means of a known method, preferably by the use of an extruder in molten state.

It is advantageous to prepare the high molecular compound in advance from the standpoint of the ease of the reaction between the components (b) and (c). On the other hand, objective polystyrene composition according to the present invention can be obtained by simultaneously melt-kneading the components (a) to (d) without being restricted to the aforementioned method.

It is desirable that the components (b) and (c) be reacted in advance with each other, and the reaction procedure between them is exemplified by the following.

(1) Reaction among a modified SPS/a rubbery elastomer/a crosslinking agent:

The high molecular compound comprising the components (b) and (c) can be produced by adding usually 0.1 to 5 parts by weight of a known crosslinking agent to 100 parts by weight of the mixture of 5 to 95% by weight of a modified SPS as the component (b) and 95 to 5% by weight of a rubbery elastomer as the component (c), while about 0.01 to 1 part by weight of a radical generating agent may be added to the reaction system to accelerate the reaction. A syndiotactic polystyrene may be used as the component (b) without limitation and is preferably exemplified by styrene/p-methylstyrene copolymer and styrene/divinylbenzene copolymer.

The usable crosslinking agent is exemplified by but not limited to sulfur, sulfur compounds such as tetrathium disulfide and multifunctional vinyl monomers such as divinylbenzene and trimethylolpropane trimethacrylate.

(2) Reaction among a modified SPS/a modified rubber/a crosslinking agent:

The high molecular compound comprising the component (b) and (c) can be produced by adding usually 0.1 to

100 parts by weight of a multifunctional compound reactive with each of the functional groups to 100 parts by weight of the mixture of 5 to 95% by weight of a modified SPS as the component (b) and 95 to 5% by weight of a rubbery elastomer as the component (c). The preferably usable component (b) include SPS modified with glycidyl methacrylate or maleic anhydride at an end, sulfonated SPS, maleic anhydride-modified SPS and glycidyl methacrylate-grafted SPS.

5 The usable multifunctional compound is exemplified by but not limited to, provided that it is reactive with the functional groups of both the modified SPS and the modified rubber, polyfunctional amines such as hexamethylenediamine and polyethylene imine, polyfunctional amides such as ethylenebisamide, nylon oligomer and polyamide dicarboxylic acid such as succinic acid and adipic acid, diol such as 1,4-butanediol, ethylene glycol and bisphenol A, glycidyl alcohol, amine acid and glycidyl ether of bisphenol A.

10 (3) Reaction between a modified SPS/a modified rubber:

The high molecular compound comprising the component (b) and (c) can be produced by reacting 5 to 95% by weight of a modified SPS as the component (b) with 95 to 5% by weight of a modified rubbery elastomer as the component (c).

The combination of functional groups of a modified SPS and a modified rubber is not limited provided that they are reactive with each other, and exemplified by the combination of an acid anhydride and an epoxy group or an amino group as a desirable one. A catalyst may be added to the reaction system to accelerate the reaction between the functional groups.

20 The above-mentioned combination is specifically exemplified by but not limited to the combination of maleic anhydride-modified SPS and an epoxy group-modified SEBS, an epoxy group-modified EPR, an amino group modified SEBS or an amino group-modified EPR and that of an epoxy group-modified SPS and a maleic anhydride-modified SEBS or a maleic anhydride-modified EPR.

In the second and fourth aspects of the present invention, the high molecular compound comprising the components (b) and (c), is employed for the purpose of the compatibilizer, and a rubbery elastomer is blended as the component (d) to improve impact resistance.

30 Examples of the rubbery elastomer include natural rubber, polybutadiene, polyisoprene, polyisobutylene, neoprene, polysulfide rubber, thiokol rubber, acrylic rubber, urethane rubber, silicone, rubber, epichlorohydrin rubber, styrene/butadiene block copolymer (SBR), a styrene/butadiene/styrene block copolymer (SBS), hydrogenated styrene/butadiene/styrene block copolymer (SEBS), styrene/isoprene block/styrene block copolymer (SIS) hydrogenated styrene/isoprene block/styrene block copolymer (SEPS), ethylene/propylene rubber (EPR), ethylene/propylene/diene rubber (EPDM) and modified rubbers therefrom.

Among the above-mentioned elastomers, SEBS, SBR, SBS, SEPS and SIS are preferably used in particular.

35 In the second and fourth aspects of the present invention, the rubbery elastomer as the component (d) is used in an amount of 1 to 100 parts by weight based on 100 parts by weight of the SPS-based resin component comprising the components (a) and (b). An amount thereof less than 1 part by weight brings about insufficient effect on improving impact resistance, while that more than 100 parts by weight causes undesirable decrease in heat resistance and rigidity due to the rubbery elastomer.

40 In the third and fourth aspects of the present invention, an inorganic filler is blended as the component (e). The inorganic filler may be in any of the forms including fiber, granule and powder.

Examples of fibrous fiber include glass fiber, carbon fiber and whisker in the form of cloth, mat, bound and cut fiber, short fiber filament, whisker, etc. There is preferably used the bound and cut fiber having a length of 0.05 to 50 mm and a diameter of 5 to 20 μm .

45 Examples of granular or powdery filler include talc, carbon black, graphite, titanium oxide, silica, mica, calcium carbonate, calcium sulfate, barium carbonate, magnesium carbonate, magnesium sulfate, barium sulfate, oxysulfate, tin oxide, alumina, kaolin, silicon carbide, metallic powder, glass powder, glass flake and glass bead.

Among the above-mentioned various inorganic fillers are particularly desirable glassy fillers including glass powder, glass flake, glass bead, glass filament, glass fiber, glass roving and glass mat.

50 The above-mentioned filler is preferably surface-treated. The coupling agent to be used for the surface treatment is to improve adhesion between the filler and resin, and may be optionally selected for use from the publicly known silane-based coupling agent and titanium-based coupling agent. Examples of the preferably usable coupling agents among them include aminosilane such as γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane and β -(3,4-epoxy-cyclohexyl) ethyltrimethoxysilane, epoxysilane and isopropyltri aminoethyl titanate.

55 In the third and fourth aspects of the present invention, the inorganic filler as the component (e) is blended in an amount of 1 to 350, preferably 5 to 200 parts by weight based on 100 parts by weight of the SPS-based resin component comprising the component (a) and (b). An amount thereof less than 1 part by weight leads to failure to sufficiently exert the blending effect as a filler, whereas that more than 350 parts by weight gives rise to the disadvantage that the

dispersibility thereof is worsened, thereby making it difficult to mold the composition.

The resin composition according to the present invention may be blended with, as desired, an additive such as antioxidant and nucleating agent or an other thermoplastic resin to the extent that the object of the present invention is not impaired. Further in the third and fourth aspects of the present invention about 0.1 to 5 parts by weight of maleic anhydride-modified polyphenylene ether per 100 parts by weight of the SPS-based resin composition comprising the component (a) and (b) may be blended in order to improve the adhesiveness between the inorganic filler as the component (e) and the resin.

The polystyrene composition thus prepared is characterized by the following.

In the first aspect of the present invention, the composition is markedly improved in impact strength and elongation by the use of the high molecular compound formed through the reaction between the components (b) and (c), as compared with the binary system of SPS/rubbery elastomer. The compound also decreases the change in physical properties arising from kneading and molding conditions and deterioration of physical properties during recycling.

In the second aspect thereof, the composition is remarkably improved in impact resistance and elongation without detriment to heat resistance and modulus of elasticity by virtue of the use of the high molecular compound formed through the reaction between the components (b) and (c) as the compatibilizer between the components (a) and (d), as compared with the simple blend of the components (a) and (d). In addition, the compatibilizer contributes to the economical efficiency due to the small usage of the component (c) and decreases the change in physical properties arising from kneading and molding conditions as well as deterioration of physical properties during recycling.

In the third aspect thereof, the composition is markedly improved in impact strength and elongation without detriment to modulus of elasticity and heat distortion temperature by the addition of the high molecular compound formed through the reaction between the components (b) and (c), as compared with the simple blend of the components (a) and (e).

In the fourth aspect thereof, the composition is improved in impact strength and elongation without detriment to modulus of elasticity and heat distortion temperature by the use of the high molecular compound formed through the reaction between the components (b) and (c) as the compatibilizer, as compared with the ternary system of the components (a), (d) and (e). Moreover, the compound as the compatibilizer contributes to the economical efficiency due to the small usage of the component (c).

In summary, the polystyrene composition according to the present invention is a syndiotactic polystyrene composition remarkably improved in impact resistance and elongation without detriment to heat resistance and modulus of elasticity, and is favorably used for molding industrial materials including electric and electronic materials such as connectors and print circuit board; industrial construction materials; automobile parts such as connectors to be mounted on vehicles, wheel cap and cylinder head cover; domestic electrical appliances and various machine parts.

In the following, the present invention will be described in more detail with reference to examples and comparative examples.

Reference Example 1

In a 2 L (L=liter) reaction vessel were placed 1 L of purified styrene, 0.1 L of p-methylstyrene, methylaluminoxane in an amount of 5 mmol as aluminum atom, 5 mmol of triisobutylaluminum and 0.025 mmol of pentamethylcyclopentadienyltitanium trimethoxide, which were then subjected to polymerization reaction at 90°C for 5 hours. After the completion of the reaction, the catalytic components were decomposed with a solution of sodium hydroxide in methanol and then the reaction product was washed with methanol repeatedly and dried to afford 320g of polymer. As the result of analysis by gel permeation chromatography using 1,2,4-trichlorobenzene at 130°C as the solvent, the polymer thus produced had a weight-average molecular weight of 390,000 and a ratio of weight-average molecular weight to number-average molecular weight of 2.60.

It was confirmed that the polymer was polystyrene having syndiotactic configuration (SPS) containing p-methylstyrene unit of 12 mol % from the results of melting point measurement and ¹³C-NMR analysis using carbon isotope.

Reference Example 2

In a 2 L reaction vessel were placed 1.0 L of purified styrene, 0.01 L of divinylbenzene, methylaluminoxane in an amount of 5 mmol as aluminum atom, 5 mmol of triisobutylaluminum and 0.025 mmol of pentamethylcyclopentadienyltitanium trimethoxide, which were then subjected to polymerization reaction at 90°C for 5 hours. After the completion of the reaction, the catalytic components were decomposed with a solution of sodium hydroxide in methanol and then the reaction product was washed with methanol repeatedly and dried to afford 320g of polymer. As the result of analysis by gel permeation chromatography using 1,2,4-trichlorobenzene at 130°C as the solvent, the polymer thus produced had a weight-average molecular weight of 385,000 and a ratio of weight-average molecular weight to number-average molecular weight of 2.55.

It was confirmed that the polymer was polystyrene having syndiotactic configuration (SPS) containing divinylbenzene unit of 1 mol% from the results of melting point measurement and ^{13}C -NMR analysis using carbon isotope.

Reference Example 3

In a 5 L reaction vessel were placed 1.2 L of purified styrene, 2.4 L of toluene, methylaluminoxane in an amount of 30 mmol as aluminum atom, 30 mmol of triisobutylaluminum and 0.15 mmol of pentamethylcyclopentadienyltitanium trimethoxide, which were then subjected to polymerization reaction at 80°C for 1 hour, followed by further polymerization reaction at 80°C for 1 hour with the addition of 50 ml of glycidyl methacrylate. After the completion of the reaction, the catalytic components were decomposed with a solution of sodium hydroxide in methanol and then the reaction product was washed with methanol repeatedly and dried to afford 360g of polymer. As the result of analysis by gel permeation chromatography using 1,2,4-trichlorobenzene at 130°C as the solvent, the polymer thus produced had a weight-average molecular weight of 253,000 and a ratio of weight-average molecular weight to number-average molecular weight of 2.60.

It was confirmed that the polymer was polystyrene having syndiotactic configuration (SPS) the end of which was modified with glycidyl methacrylate from the results of melting point measurement and ^{13}C -NMR analysis using carbon isotope.

Reference Example 4

In a 2 L reaction vessel were placed 100g of SPS as obtained in Reference Example 2, 500 ml of toluene, 10 ml of glycidyl methacrylate and 1g of azobis(isobutyronitrile) which were then subjected to modification reaction at 80°C for 5 hours. After the completion of the reaction, the reaction product was washed with methanol repeatedly and dried to afford 110g of polymer, which was subjected to Soxhlet extraction using methyl ethyl ketone, and IR analysis. As a result, the introduction of glycidyl methacrylate was confirmed.

Reference Example 5

100 parts by weight of SPS in Reference Example 1, 3 parts by weight of maleic anhydride and 1 part by weight of 2,3-dimethyl-2,3-diphenylbutane (produced by Nippon Oil & Fat Co., Ltd. under the tradename "NOPHMER BC") were dry-blended and melt kneaded by the use of a 30 mm twin-screw extruder at a revolution of 200 rpm at a temperature set to 300°C, while the resin temperature was about 330°C. The resultant strand was cooled and then pelletized to produce maleic anhydride-modified SPS.

In order to measure the modification rate, 1g of the resultant modified SPS was dissolved chloroform and thereafter reprecipitated in methanol, and the recovered polymer was subjected to Soxhlet extraction using methanol and dried. The modification rate was determined from the intensity of carbonyl absorption in infrared (IR) absorption spectrum.

Preparation Example 1

50 parts by weight of SPS in Reference Example 1, 50 parts by weight of SEBS (produced by Shell Chem. Co. under the tradename "Kraton G-1651"), 3 parts by weight of maleic anhydride as the crosslinking agent and 1 part by weight of 2,3-dimethyl-2,3-diphenylbutane (produced by Nippon Oil & Fat Co., Ltd. under the tradename "NOPHMER BC") as the radical generating agent were dry-blended and melt kneaded by the use of a 30 mm twin-screw extruder at revolution of 200 rpm at a temperature set to 300°C. The resultant strand was cooled and then pelletized to produce SEBS/SPS graft copolymer. The resultant copolymer was subjected to Soxhlet extraction using hexane as the solvent to remove the residual SEBS and was dried. The graft copolymerization of SEBS and SPS was confirmed by the weight of the hexane-insoluble portion and ^1H -NMR analysis.

Preparation Examples 2 to 19

The procedure in Preparation Example 1 was repeated except that the kinds of modified SPS and rubbery elastomers, SPS/rubbery elastomer ratio, and the kinds and amounts of crosslinking agents and radical generating agents were altered as given in Table 1.

Table 1

		(b)		(c)		Others(crosslinking agent, radical generating agent)	
		Kind	Part/s by weight	kind	Part/s by weight	kind	Part/s by weight
5	Preparation Example 1	Reference Example 1	10	G-1651 ¹⁾	90	maleic anhydride	1
10						NOPHMER BC ⁶⁾	0.1
	Preparation Example 2	Reference Example 1	50	G-1651	50	maleic anhydride	3
15						NOPHMER BC	0.1
	Preparation Example 3	Reference Example 2	10	NS-312S ²⁾	90	NOPHMER BC	0.1
20	Preparation Example 4	Reference Example 2	50	NS-312S	50	NOPHMER BC	0.1
	Preparation Example 5	Reference Example 2	10	G-1651	90	maleic anhydride	3
25						NOPHMER BC	0.1
	Preparation Example 6	Reference Example 2	50	G-1651	50	maleic anhydride	3
30						NOPHMER BC	0.1
	Preparation Example 7	Reference Example 3	10	M-1913 ³⁾	90	none	-
35	Preparation Example 8	Reference Example 3	50	M-1913	50	none	-
	Preparation Example 9	Reference Example 3	10	T-7711SP ⁴⁾	90	none	-
40	Preparation Example 10	Reference Example 3	50	T-7711SP	50	none	-
45	Preparation Example 11	Reference Example 4	10	M-1913	90	none	-
50	Preparation Example 12	Reference Example 4	50	M-1913	50	none	-

Remarks 1) SEBS produced by Shell Chem. Co.

2) SBR produced by Nippon Zeon Co., Ltd.

3) maleic anhydride-modified SEBS produced by Asahi Chemical Industry Co., Ltd.

4) maleic anhydride-modified EPR produced by Japan Synthetic Rubber Co., Ltd.

6) 2,3-dimethyl-2,3-diphenylbutane produced by Nippon Oil & Fat Co., Ltd.

Table 1 (continued)

	(b)		(c)		Others(crosslinking agent, radical generating agent)	
	Kind	Part/s by weight	kind	Part/s by weight	kind	Part/s by weight
Preparation Example 13	Reference Example 5	10	Z-513 ⁵⁾	90	none	-
Preparation Example 14	Reference Example 5	50	Z-513	50	none	-
Preparation Example 15	Reference Example 5	80	Z-513	20	none	-
Preparation Example 16	Reference Example 5	90	Z-513	10	none	-
Preparation Example 17	Reference Example 5	95	Z-513	5	none	-
Preparation Example 18	Reference Example 5	50	M-1913	50	hexamethylenediamine	0.1
Preparation Example 19	Reference Example 5	50	M-1913	50	EPICHLON-50 ⁷⁾	0.5

5) epoxy group-modified SEBS produced by Asahi Chemical Industry Co., Ltd.

7) epoxy resin, type bisphenol A produced by Daiippon Ink & Chemicals, Inc.

8) oligo amide produced by Kyoeisha Chemical Co., Ltd.

Example 1

To 97.2 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, as the component (b)+(c), 27.8 parts by weight of the product in Preparation Example 1, 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Daiippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 2.

Example 2-10

The procedure in Example 1 was repeated except that the amount of the component (a) and the kind and amount of the component (b)+(c) were altered as given in Table 2. The result are given in Table 2.

Example 11

To 95 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 5 parts by weight of the product in Reference Example 5 as the component (b), 25 parts by weight of epoxy group-modified SEBS (Z-513, produced by Asahi Chemical Industry Co., Ltd.) as the component (c), 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Daiippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by

weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methlene-3-(3',5'-di-tert-butyl-4'-hydroxy-phenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 2.

Examples 12

The procedure in Example 11 was repeated except that the component (b) was used in an amount of 100 parts by weight and the component (a) was not used. The results are given in Table 2.

Example 13

The procedure in Example 11 was repeated except that there were used 25 parts by weight of maleic anhydride-modified SEBS (M-1913, produced by Asahi Chemical Industry Co., Ltd.) as the component (c) and 0.5 part by weight of epoxy resin, type bisphenol A (EPICHLON-50, produced by Dainippon Ink & Chemicals, Inc.) as the crosslinking agent for the components (b) and (c). The results are given in Table 2.

Comparative Examples 1-7

The procedure in Example 1 was repeated except that there were used the respective products as the component (c) as shown in Table 2 for the kind and the amount based on 100 parts by weight of the SPS without the use of the component (b). The results are given in Table 2.

As is clear from Table 2, the use of the high molecular compound comprising modified SPS and the rubbery elastomer in the objective SPS composition makes it possible to remarkably improve its impact strength and elongation without detriment to its modulus of elasticity and heat distortion temperature as compared with the rubbery elastomer alone without SPS. In addition, as is demonstrated in Examples 11 to 13, it is possible to produce the objective resin composition by simultaneously kneading each of the components for preparing the components (a) and (b)+(c), respectively.

Table 2-1

	(a)		[(b) (c)]	
	Amount added (part/s by weight)	kind	Amount added (part/s by weight)	
5	Example 1	97.2	Preparation Example 1	27.8
	Example 2	98.8	Preparation Example 1	12.2
10	Example 3	97.2	Preparation Example 3	27.8
	Example 4	97.2	Preparation Example 5	27.8
	Example 5	97.2	Preparation Example 7	27.8
15	Example 6	97.2	Preparation Example 9	27.8
	Example 7	97.2	Preparation Example 11	27.8
	Example 8	97.2	Preparation Example 13	27.8
20	Example 9	75.0	Preparation Example 14	50.0
	Example 10	-	Preparation Example 15	100.0
25	Example 11	95.0	Reference Example 5 Z-513	5.0 25.0
	Example 12	-	Reference Example 5 Z-513	100.0 25.0
30	Example 13	95.0	Reference Example 5 M-1913 EPICHLON-50	5.0 25.0 0.5
(c)				
35	Comparative Example 1	100	G-1651	25.0
	Comparative Example 2	100	G-1651	11.0
40	Comparative Example 3	100	NS-312S	25.0
	Comparative Example 4	100	M-1913	25.0
45	Comparative Example 5	100	EP-912P	25.0
	Comparative Example 6	100	T-7711SP	25.0
50	Comparative Example 7	100	Z-513	25.0

55

Table 2-2

	Izod impact strength with notch ¹⁾ (kj/m ²)	Elongation ²⁾ (%)	Flexural modulus of elasticity ³⁾ (MPa)	Heat distortion temperature ⁴⁾ (°C)	
5	Example 1	11.5	19.1	2540	130
10	Example 2	7.0	10.0	3700	146
	Example 3	14.2	21.0	2490	131
	Example 4	13.1	18.7	2500	132
15	Example 5	15.5	20.1	2510	132
	Example 6	8.7	9.8	2100	117
20	Example 7	15.8	19.3	2510	135
	Example 8	15.5	20.5	2550	133
	Example 9	16.1	22.4	2530	133
25	Example 10	17.1	25.1	2560	135
	Example 11	14.1	18.5	2570	131
	Example 12	16.0	21.0	2510	135
30	Example 13	14.8	18.1	2550	134
	Comparative Example 1	5.2	11.1	2470	125
35	Comparative Example 2	2.8	2.0	3580	140
	Comparative Example 3	8.5	15.0	2500	130
40	Comparative Example 4	6.0	11.0	2520	131
	Comparative Example 5	3.9	6.9	2100	118
45	Comparative Example 6	4.0	5.8	2150	120
50	Comparative Example 7	5.8	13.8	2540	126
<hr/>					
	Remarks 1) according to JIS K-7110				
	2) according to JIS K-7113				
55	3) according to JIS K-7203				
	4) according to JIS K-7207				

Example 14

To 98 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 4 parts by weight of the high molecular compound in Preparation Example 2 as the compatibilizer component (b)+(c), 23 parts by weight of SEBS (Kraton G-1651, produced by Shell Chem. Co.), 1 part by weight of p-(tert-butyl) aluminum benzoate (produced by Dainippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 3.

Examples 15-25

The procedure in Example 14 was repeated except that the amount of the component (a) and the kinds and amounts of the component (b)+(c) and the component (d) were altered as given in Table 3. The results are given in Table 3.

Example 26

To 97 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 3 parts by weight of the product in Reference Example 5 as the component (b), 3 parts by weight of epoxy group-modified SEBS (Z-513, produced by Asahi Chemical Industry Co., Ltd.) as the component (c), 22 parts by weight of SEBS (Kraton G-1651, produced by Shell Chem. Co.) as the component (d), 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Dainippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 3.

Examples 27-29

The procedure in Example 26 was repeated except that there were used maleic anhydride-modified SEBS (M-1913, produced by Asahi Chemical Industry Co., Ltd.) as the component (c) in respective amounts given in Table 3 and 0.1 part by weight of epoxy resin, type bisphenol A (EPICHLON-50, produced by Dainippon Ink & Chemicals, Inc.) as the crosslinking agent for the components (b) and (c). The results are given in Table 3.

As is clear from Table 3, the use of the high molecular compound comprising modified SPS and the rubbery elastomer as the compatibilizer in the objective SPS composition makes it possible to remarkably improve its impact strength and elongation without detriment to its modulus of elasticity and heat distortion temperature as compared with the rubbery elastomer alone without SPS as shown in Table 2 on the columns of Comparative Examples 1-7. In addition, as is demonstrated in Examples 26-29, it is possible to produce the objective resin composition by simultaneously kneading each of the components for preparing the components (a) and (b)+(c), respectively.

Table 3-1

	(a)		[(b) + (c)]		(d)
	Amount added		Amount added		Amount added
	(part/s by weight)	Kind	(part/s by weight)	kind	(part/s by weight)
5					
	Example 14	98	Preparation Example 2	4	G-1651 23
10					
	Example 15	98	Preparation Example 4	4	NS-312S 23
	Example 16	98	Preparation Example 6	4	G-1651 23
15					
	Example 17	98	Preparation Example 8	4	G-1651 23
	Example 18	98	Preparation Example 10	4	EP-912P 23
20					
	Example 19	98	Preparation Example 12	4	G-1651 23
	Example 20	98	Preparation Example 14	4	G-1651 23
25					
	Example 21	98	Preparation Example 14	4	G-1651 9
	Example 22	84	Preparation Example 15	20	G-1651 21
30					
	Example 23	-	Preparation Example 16	111	G-1651 14
	Example 24	90	Preparation Example 18	20	G-1651 15
35					
	Example 25	80	Preparation Example 19	40	G-1651 5
	Example 26	97	Reference Example 5 M-513	3 3	G-1651 22
40					
	Example 27	90	Reference Example 5 M-1913 EPICHLON-50	10 5 0.1	G-1651 20
45					
	Example 28	-	Reference Example 5 M-1913 EPICHLON-50	100 5 0.1	G-1651 20
50					
	Example 29	90	Reference Example 5 M-1913 LIGHT AMIDE WH215 ⁸⁾	10 5 3	G-1651 20
55					

Table 3-2

		Izod impact strength with notch ¹⁾ (kJ/m ²)	Elongation ²⁾ (%)	Flexural modulus of elasticity ³⁾ (MPa)	Heat distortion temperature ⁴⁾ (°C)
5					
10	Example 14	12.3	19.3	2550	130
	Example 15	14.0	20.1	2590	130
	Example 16	13.1	18.1	2510	132
15	Example 17	14.1	18.5	2500	135
	Example 18	8.5	10.0	2010	110
20	Example 19	13.2	18.1	2490	132
	Example 20	14.3	20.5	2520	133
	Example 21	7.1	10.6	3680	144
25	Example 22	14.8	21.4	2500	131
	Example 23	15.6	23.0	2600	135
30	Example 24	13.9	20.0	2490	133
	Example 25	13.5	18.1	2550	130
	Example 26	12.1	17.0	2550	131
35	Example 27	12.5	17.6	2560	131
	Example 28	15.5	23.5	2570	137
40	Example 29	13.0	18.3	2490	128

1) according to JIS K-7110

2) according to JIS K-7113

3) according to JIS K-7203

4) according to JIS K-7207

Example 30

To 98.8 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 12.2 parts by weight of the product in Preparation Example 1 as the component (b)+(c), 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Dainippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3'5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was incorporated with 43 parts by weight of glass fiber by side feeding, melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was

injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 4.

Examples 31-39

The procedure in Example 30 was repeated except that the amount of the component (a) and the kinds and amounts of the component (b)+(c) were altered as given in Table 2. The result are given in Table 4.

Example 40

To 95 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 5 parts by weight of the product in Reference Example 5 as the component (b), 11 parts by weight of epoxy group-modified SEBS (Z-513, produced by Asahi Chemical Industry Co., Ltd.) as the component (c) 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Dainippon Ink & Chemicals, Inc. under the tradename "PTBBA-AI") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3'5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was incorporated with 43 parts by weight of glass fiber by side feeding, melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 4.

Example 41

The procedure in Example 40 was repeated except that the component (b) was used in an amount of 100 parts by weight and the component (a) was not used. The results are given in Table 4.

Example 42

The procedure in Example 40 was repeated except that there were used 11 parts by weight of maleic anhydride-modified SEBS (M-1913, produced by Asahi Chemical Industry Co., Ltd.) as the component (c) and 0.5 part by weight of epoxy resin, type bisphenol A (EPICHLON-50, produced by Dainippon Ink & Chemicals, Inc.) as the crosslinking agent for the components (b) and (c). The results are given in Table 4.

Comparative Examples 8-14

The procedure in Example 30 was repeated except that there were used the respective products as the component (c) as shown in Table 4 for the kind and the amount based on 100 parts by weight of the SPS without the use of the component (b). the results are given in Table 4.

As is clear from Table 4, the use of the high molecular compound comprising modified SPS and the rubbery elastomer in the objective SPS composition makes it possible to remarkably improve its impact strength and elongation without detriment to its modulus of elasticity and heat distortion temperature as compared with the rubbery elastomer alone without SPS. In addition, as is demonstrated in Examples 40 to 42, it is possible to produce the objective resin composition by simultaneously kneading each of the components for preparing the components (a) and (b)+(c), respectively.

Table 4-1

5	(a)		[(b) + (c)]	
	Amount added (part/s by weight)	kind	Amount added (part/s by weight)	
	Example 30	98.8	Preparation Example 1	12.2
10	Example 31	99.4	Preparation Example 1	5.6
	Example 32	98.8	Preparation Example 3	12.2
	Example 33	98.8	Preparation Example 5	12.2
15	Example 34	98.8	Preparation Example 7	12.2
	Example 35	98.8	Preparation Example 9	12.2
	Example 36	98.8	Preparation Example 11	12.2
20	Example 37	98.8	Preparation Example 13	12.2
	Example 38	89.0	Preparation Example 14	22.0
	Example 39	-	Preparation Example 16	111.0
25	Example 40	95.0	Reference Example 5 Z-513	5.0 11.0
	Example 41	-	Reference Example 5 Z-513	100.0 11.0
30	Example 42	95.0	Reference Example 5 M-1913 EPICHLON-50	5.0 11.0 0.5
(c)				
35	Comparative Example 8	100	G-1651	5.0
	Comparative Example 9	100	G-1651	11.0
40	Comparative Example 10	100	NS-312S	11.0
	Comparative Example 11	100	M-1913	11.0
45	Comparative Example 12	100	EP-912P	11.0
	Comparative Example 13	100	T-7711SP	11.0
50	Comparative Example 14	100	Z-513	11.0

55

Table 4-2

		Izod impact strength with notch ¹⁾ (kj/m ²)	Elongation ²⁾ (%)	Flexural modulus of elasticity ³⁾ (MPa)	Heat distortion temperature ⁴⁾ (°C)
5	Example 30	11.8	2.9	8680	243
10	Example 31	8.9	2.0	9700	239
	Example 32	14.7	2.8	8780	230
	Example 33	14.9	2.9	8720	244
15	Example 34	13.1	2.9	8650	230
	Example 35	10.1	2.0	8050	215
	Example 36	13.1	2.9	8660	225
20	Example 37	14.2	2.7	8750	226
	Example 38	15.5	2.8	8710	226
25	Example 39	16.3	3.0	8660	230
	Example 40	13.3	2.7	8700	231
	Example 41	15.0	2.9	8710	229
30	Example 42	13.0	2.7	8750	229
	Comparative Example 8	3.8	1.0	9750	230
35	Comparative Example 9	4.1	1.0	8600	221
	Comparative Example 10	3.1	1.0	8710	222
40	Comparative Example 11	4.2	1.2	8720	225
	Comparative Example 12	3.1	1.0	8430	210
45	Comparative Example 13	3.9	1.1	8480	210
	Comparative Example 14	4.8	1.3	8700	223
50					

Remarks 1) according to JIS K-7110
 2) according to JIS K-7113
 3) according to JIS K-7203
 4) according to JIS K-7207

Example 43

To 98 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 4 parts by weight of the high molecular compound obtained in Preparation Example 2 as the compatibilizer [(b)+(c)], 9 parts by weight of SEBS (Kraton G-1651, produced by Shell Chem. Co.), 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Dainippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3'5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 5.

Examples 44-53

The procedure in Example 43 was repeated except that the amount of the component (a) and the kinds and amounts of the component (b)+(c) and the component (d) were altered as given in Table 5. The result are given in Table 5.

Example 54

To 97 parts by weight of syndiotactic polystyrene (SPS, weight-average molecular weight of 305,000, weight-average molecular weight Mw/number-average molecular weight Mn of 2.35) were added, 3 parts by weight of the product in Reference Example 5 as the component (b), 3 parts by weight of epoxy group-modified SEBS (Z-513, produced by Asahi Chemical Industry Co., Ltd.) as the component (c), 8 parts by weight of SEBS (Kraton G-1651, produced by Shell Chem. Co.) as the component (d), 1 part by weight of p-(tert-butyl)aluminum benzoate (produced by Dainippon Ink & Chemicals, Inc. under the tradename "PTBBA-Al") as the nucleating agent; 0.1 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (produced by Adeka Argus Co., Ltd. under the tradename "PEP-36") as an antioxidant and 0.1 part by weight of tetrakis [methylene-3-(3'5'-di-tert-butyl-4'-hydroxyphenyl)] propionate (produced by Adeka Argus Co., Ltd. under the tradename "MARK A060") also as an antioxidant, and the resultant mixture was blended with a Henschel mixer. Subsequently the blend was melt kneaded and pelletized with a twin-screw extruder. The pellet thus obtained was injection molded to produce test pieces for tensile test, flexural test and Izod impact test, respectively. Measurements were made of Izod impact strength, elongation, modulus of elasticity and heat distortion temperature of the test pieces thus obtained. The results are given in Table 5.

Example 55-57

The procedure in Example 54 was repeated except that there were used maleic anhydride-modified SEBS (M-1913, produced by Asahi Chemical Industry Co., Ltd.) as the component (c) in respective amounts given in Table 5 and 0.1 part by weight of epoxy resin, type bisphenol A (EPICHLON-50, produced by Dainippon Ink & Chemicals, Inc.) as the crosslinking agent for the components (b) and (c). The results are given in Table 5.

As is clear from Table 5, the use of the high molecular compound comprising modified SPS and the rubbery elastomer as the compatibilizer in the objective SPS composition makes it possible to remarkably improve its impact strength and elongation without detriment to its modulus of elasticity and heat distortion temperature as compared with the rubbery elastomer alone without SPS as shown in Table 4 on the columns of Comparative Examples 8-14. In addition, as is demonstrated in Examples 54-57, it is possible to produce the objective resin composition by simultaneously kneading each of the components for preparing the components (a) and (b)+(c), respectively.

Table 5.1

	(a)		[(b) + (c)]		(d)	
5	Amount added (part/s by weight)		Preparation Example	Amount added (part/s by weight)	kind	Amount added (part/s by weight)
	Example 43	98	Preparation Example 2	4	G-1651	9
10	Example 44	98	Preparation Example 4	4	NS-312S	3
	Example 45	98	Preparation Example 6	4	G-1651	9
15	Example 46	98	Preparation Example 8	4	G-1651	9
	Example 47	98	Preparation Example 10	4	EP-912P	9
20	Example 48	98	Preparation Example 12	4	G-1651	9
	Example 49	98	Preparation Example 14	4	G-1651	9
25	Example 50	84	Preparation Example 15	20	G-1651	7
30	Example 51	-	Preparation Example 17	105.3	G-1651	5.7
	Example 52	98	Preparation Example 18	4	G-1651	9
35	Example 53	98	Preparation Example 19	4	G-1651	9
	Example 54	97	Reference Example 5 M-513	3 3	G-1651	8
40	Example 55	90	Reference Example 5 M-1913 EPICHLON-50	10 5 0.1	G-1651	6
45	Example 56	-	Reference Example 5 M-1913 EPICHLON-50	100 5 0.1	G-1651	6
50	Example 57	90	Reference Example 5 M-1913 LIGHT AMIDE WH 215 ⁸⁾	10 5 3	G-1651	6

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Table 5-2

	Izod impact strength with notch ¹⁾ (kJ/m ²)	Elongation ²⁾ (%)	Flexural modulus of elasticity ³⁾ (MPa)	Heat distortion temperature ⁴⁾ (°C)
Example 43	11.0	2.7	8680	241
Example 44	14.0	2.9	8650	230
Example 45	13.1	2.7	8690	240
Example 46	13.5	2.9	8700	228
Example 47	9.7	2.0	8010	213
Example 48	13.0	2.8	8710	231
Example 49	13.8	2.9	8750	232
Example 50	15.0	2.9	8700	229
Example 51	14.9	2.8	8720	228
Example 52	14.8	2.9	8710	230
Example 53	13.0	2.7	8650	230
Example 54	13.0	2.7	8690	229
Example 55	13.2	2.8	8650	231
Example 56	14.8	2.9	8700	231
Example 57	13.4	2.9	8590	228

1) according to JIS K-7110

2) according to JIS K-7113

3) according to JIS K-7203

4) according to JIS K-7207

Example 58

The Izod impact test pieces which had been prepared in Example 1 were crushed into small pieces, which were again made into test pieces to measure the dynamical properties thereof. The results are given in Table 6.

Examples 59-65 and Comparative Examples 15-19

The procedure in Example 58 was repeated except that there were used the Izod impact test pieces as shown in Table 6 on the columns of Examples 3, 6, 8, 14, 15, 18 and 20 and those of Comparative Examples 1, 3, 5, 6, and 7, respectively. The results are given Table 6.

As is clear from Table 6, the resin composition of the present invention comprising the high molecular compound consisting essentially of the modified SPS as the component (b) and the rubbery elastomer as the component (c) is

not considerably deteriorated in physical properties owing to recycling, thus making itself practically useful.

Table 6

Test piece	used	Change in Izod impact strength with the number of recycles (KJ/m ²) ¹⁾				
		once	twice	thrice	four times	five times
Example 58	Example 1	11.5	10.5	9.8	9.2	8.9
Example 59	Example 3	14.2	13.0	11.9	11.3	10.8
Example 60	Example 6	8.7	7.0	6.2	5.8	5.6
Example 61	Example 8	15.5	14.2	13.2	12.5	12.0
Example 62	Example 14	12.3	11.0	9.9	9.0	8.7
Example 63	Example 15	14.0	12.8	12.0	10.9	10.0
Example 64	Example 18	8.5	7.2	6.1	5.8	5.5
Example 65	Example 20	14.3	13.0	12.3	12.0	11.5
Comparative Example 15	Comparative Example 1	5.2	3.2	2.4	2.1	1.8
Comparative Example 16	Comparative Example 3	8.5	6.1	4.0	3.2	2.8
Comparative Example 17	Comparative Example 5	3.9	2.8	2.1	1.8	1.6
Comparative Example 18	Comparative Example 6	4.0	2.8	2.3	1.9	1.5
Comparative Example 19	Comparative Example 7	5.8	3.8	3.0	2.5	2.3

¹⁾ according to JIS K-7110

Claims

1. A polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of a styrenic polymer having syndiotactic configuration (a) and 100 to 1% by weight of a styrenic polymer having syndiotactic configuration and a functional group (b); and 1 to 100 parts by weight of a rubbery elastomer which can react with said functional group of the component (b) as the component (c), said resin component (a) + (b) and component (c) being blended with each other, wherein the component (b) and the component (c) are constituting a high molecular compound prepared by reaction.
2. A polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of a styrenic polymer having syndiotactic configuration (a) and 100 to 1% by weight of a styrenic polymer having syndiotactic configuration and a functional group (b); 1 to 10 parts by weight of a rubbery elastomer which can react with said functional group of the component (b) as the component (c); and 1 to 100 parts by weight of a rubbery elastomer (d), said resin component (a)+(b) and components (c) and (d) being blended with each other wherein the component (b) and the component (c) are constituting a high molecular compound prepared by reaction.
3. A polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of a styrenic polymer having syndiotactic configuration (a) and 100 to 1% by weight of a styrenic polymer having syndiotactic configuration and a functional group (b); 1 to 100 parts by weight of a rubbery elastomer which can react with said functional group of the component (b) as the component (c); and 1 to 350 parts by weight of an inorganic filler (e), said resin component (a)+(b) and components (c) and (e) being blended with each other, wherein the component (b) and the component (c) are constituting a high molecular compound prepared by reaction.
4. A polystyrene composition which comprises 100 parts by weight of a resin component comprising 0 to 99% by weight of a styrenic polymer having syndiotactic configuration (a) and 100 to 1% by weight of a styrenic polymer having syndiotactic configuration and a functional group (b); 1 to 10 parts by weight of a rubbery elastomer which can react with said functional group of the component (b) as the component (c); 1 to 100 parts by weight of a

rubbery elastomer (d), and 1 to 350 parts by weight of an inorganic filler (e), said resin component (a)+(b) and components (c), (d) and (e) being blended with each other, wherein the component (b) and the component (c) constituting a high molecular compound prepared by reaction.

- 5 5. The composition according to Claim 1 wherein the rubbery elastomer as the component (c) is selected from the group consisting of hydrogenated styrene/butadiene/styrene copolymer rubber (SEBS), styrene/butadiene/styrene copolymer rubber (SBS), styrene/butadiene copolymer rubber (SBR), ethylene/propylene copolymer rubber (EPR) and modified rubbers therefrom.
- 10 6. The composition according to Claim 2 wherein the rubbery elastomer as the component (c) is selected from the group consisting of SEBS, SBS, SBR, EPR and modified rubbers therefrom.
7. The composition according to Claim 3 wherein the rubbery elastomer as the component (c) is selected from the group consisting of SEBS, SBS, SBR, EPR and modified rubbers therefrom.
- 15 8. The composition according to Claim 4 wherein the rubbery elastomer as the component (c) is selected from the group consisting of SEBS, SBS, SBR, EPR and modified rubbers therefrom.
9. The composition according to Claim 2 wherein the rubbery elastomer as the component (d) is selected from the group consisting of SEBS, SBS, SBR and EPR.
- 20 10. The composition according to Claim 4 wherein the rubbery elastomer as the component (d) is selected from the group consisting of SEBS, SBS, SBR, and EPR.
- 25 11. The composition according to Claim 3 wherein the inorganic filler as the component (e) is glass fiber.
12. The composition according to Claim 4 wherein the inorganic filler as the component (e) is glass fiber.

30 Patentansprüche

1. Polystyrolzusammensetzung, die umfaßt: 100 Gewichtsteile einer Harzkomponente, die 0 bis 99 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration (a) und 100 bis 1 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration und einer funktionellen Gruppe (b) umfaßt; und 1 bis 100 Gewichtsteile eines kautschukartigen Elastomers, das mit der erwähnten funktionellen Gruppe der Komponente (b) reagieren kann, als Komponente (c), wobei die genannten Harzkomponenten (a) + (b) und die Komponente (c) miteinander vermischt werden und die Komponente (b) und die Komponente (c) durch Reaktion eine hochmolekulare Verbindung bilden.
2. Polystyrolzusammensetzung, die umfaßt: 100 Gewichtsteile einer Harzkomponente, die 0 bis 99 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration (a) und 100 bis 1 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration und einer funktionellen Gruppe (b) umfaßt; 1 bis 10 Gewichtsteile eines kautschukartigen Elastomers, das mit der erwähnten funktionellen Gruppe der Komponente (b) reagieren kann, als Komponente (c); und 1 bis 100 Gewichtsteile eines kautschukartigen Elastomers (d), wobei die genannten Harzkomponenten (a) + (b) und die Komponenten (c) und (d) miteinander vermischt werden und die Komponente (b) und die Komponente (c) durch Reaktion eine hochmolekulare Verbindung bilden.
3. Polystyrolzusammensetzung, die umfaßt: 100 Gewichtsteile einer Harzkomponente, die 0 bis 99 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration (a) und 100 bis 1 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration und einer funktionellen Gruppe (b) umfaßt; 1 bis 100 Gewichtsteile eines kautschukartigen Elastomers, das mit der erwähnten funktionellen Gruppe der Komponente (b) reagieren kann, als Komponente (c); und 1 bis 350 Gewichtsteile eines anorganischen Füllstoffes (e), wobei die genannten Harzkomponenten (a) + (b) und die Komponente (c) und (e) miteinander vermischt werden und die Komponente (b) und die Komponente (c) durch Reaktion eine hochmolekulare Verbindung bilden.
4. Polystyrolzusammensetzung, die umfaßt: 100 Gewichtsteile einer Harzkomponente, die 0 bis 99 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration (a) und 100 bis 1 Gew.-% eines Styrolpolymers mit syndiotaktischer Konfiguration und einer funktionellen Gruppe (b) umfaßt; 1 bis 10 Gewichtsteile eines kautschukartigen Elastomers, das mit der erwähnten funktionellen Gruppe der Komponente (b) reagieren kann, als Komponente

(c); 1 bis 100 Gewichtsteile eines kautschukartigen Elastomers (d); und 1 bis 350 Gewichtsteile eines anorganischen Füllstoffes (e) wobei die genannten Harzkomponenten (a) + (b) und die Komponente (c) und (e) miteinander vermischt werden und die Komponente (b) und die Komponente (c) durch Reaktion eine hochmolekulare Verbindung bilden.

5 5. Zusammensetzung nach Anspruch 1, worin das kautschukartige Elastomer als Komponente (c) aus der Gruppe ausgewählt wird, die aus einem hydrierten Styrol/Butadien/Styrol-Copolymerkautschuk (SEBS), einem Styrol/Butadien/Styrol-Copolymerkautschuk (SBS), einem Styrol/Butadien-Copolymerkautschuk (SBR), einem Ethylen/Propylen-Copolymerkautschuk (EPR) und modifizierten Kautschuken davon besteht.

10 6. Zusammensetzung nach Anspruch 2, worin das kautschukartige Elastomer als Komponente (c) aus der Gruppe ausgewählt wird, die aus SEBS, SBS, SBR, EPR und modifizierten Kautschuken davon besteht.

15 7. Zusammensetzung nach Anspruch 3, worin das kautschukartige Elastomer als Komponente (c) aus der Gruppe ausgewählt wird, die aus SEBS, SBS, SBR, EPR und modifizierten Kautschuken davon besteht.

8. Zusammensetzung nach Anspruch 4, worin das kautschukartige Elastomer als Komponente (c) aus der Gruppe ausgewählt wird, die aus SEBS, SBS, SBR, EPR und modifizierten Kautschuken davon besteht.

20 9. Zusammensetzung nach Anspruch 2, worin das kautschukartige Elastomer als Komponente (d) aus der Gruppe ausgewählt wird, die aus SEBS, SBS, SBR, EPR und modifizierten Kautschuken davon besteht.

25 10. Zusammensetzung nach Anspruch 4, worin das kautschukartige Elastomer als Komponente (d) aus der Gruppe ausgewählt wird, die aus SEBS, SBS, SBR, EPR und modifizierten Kautschuken davon besteht.

11. Zusammensetzung nach Anspruch 3, worin es sich bei dem anorganischen Füllstoff als Komponente (e) um Glasfasern handelt.

30 12. Zusammensetzung nach Anspruch 4, worin es sich bei dem anorganischen Füllstoff als Komponente (e) um Glasfasern handelt.

Revendications

35 1. Une composition de polystyrène qui comprend 100 parties en masse d'un composant de résine comprenant 0 à 99 % en masse d'un polymère styrénique présentant une configuration syndiotactique (a) et 100 à 1 % en masse d'un polymère styrénique présentant une configuration syndiotactique et un groupe fonctionnel (b); et 1 à 100 parties en masse d'un élastomère caoutchouteux qui peut réagir avec ledit groupe fonctionnel du composant (b) en tant que composant (c), ledit composant de résine (a) + (b) et le composant (c) étant mélangés l'un avec l'autre, dans laquelle le composant (b) et le composant (c) constituent un composé de masse moléculaire élevée préparé par réaction.

40 2. Une composition de polystyrène qui comprend 100 parties en masse d'un composant de résine comprenant 0 à 99 % en masse d'un polymère styrénique présentant une configuration syndiotactique (a) et 100 à 1 % en masse d'un polymère styrénique présentant une configuration syndiotactique et un groupe fonctionnel (b); 1 à 10 parties en masse d'un élastomère caoutchouteux qui peut réagir avec ledit groupe fonctionnel du composant (b) en tant que composant (c); et 1 à 100 parties en masse d'un élastomère caoutchouteux (d), ledit composant de résine (a) + (b) et les composants (c) et (d) étant mélangés les uns avec les autres, dans laquelle le composant (b) et le composant (c) constituent un composé de masse moléculaire élevée préparé par réaction.

50 3. Une composition de polystyrène qui comprend 100 parties en masse d'un composant de résine comprenant 0 à 99 % en masse d'un polymère styrénique présentant une configuration syndiotactique (a) et 100 à 1 % en masse d'un polymère styrénique présentant une configuration syndiotactique et un groupe fonctionnel (b); 1 à 100 parties en masse d'un élastomère caoutchouteux qui peut réagir avec ledit groupe fonctionnel du composant (b) en tant que composant (c), et 1 à 350 parties en masse d'une matière de charge inorganique (e), ledit composant de résine (a) + (b) et les composants (c) et (e) étant mélangés les uns avec les autres, dans laquelle le composant (b) et le composant (c) constituent un composé de masse moléculaire élevée préparé par réaction.

4. Une composition de polystyrène qui comprend 100 parties en masse d'un composant de résine comprenant 0 à 99 % en masse d'un polymère styrénique présentant une configuration syndiotactique (a) et 100 à 1% en masse d'un polymère styrénique présentant une configuration syndiotactique et un groupe fonctionnel (b); 1 à 10 parties en masse d'un élastomère caoutchouteux qui peut réagir avec ledit groupe fonctionnel du composant (b) en tant que composant (c); 1 à 100 parties en masse d'un élastomère caoutchouteux (d); et 1 à 350 parties en masse d'une matière de charge inorganique (e), ledit composant de résine (a) + (b) et les composants (c), (d) et (e) étant mélangés les uns avec les autres, dans laquelle le composant (b) et le composant (c) constituent un composé de masse moléculaire élevée préparé par réaction
5. La composition selon la Revendication 1, dans laquelle l'élastomère caoutchouteux en tant que composant (c) est sélectionné parmi le groupe composé d'un caoutchouc copolymère styrène hydrogéné / butadiène / styrène (SEBS), d'un caoutchouc copolymère styrène / butadiène / styrène (SBS), d'un caoutchouc copolymère styrène / butadiène (SBR), d'un caoutchouc copolymère éthylène / propylène (EPR), et de caoutchoucs modifiés de ceux-ci.
6. La composition selon la Revendication 2, dans laquelle l'élastomère caoutchouteux en tant que composant (c) est sélectionné parmi le groupe composé de SEBS, SBS, SBR, EPR, et de caoutchoucs modifiés de ceux-ci.
7. La composition selon la Revendication 3, dans laquelle l'élastomère caoutchouteux en tant que composant (c) est sélectionné parmi le groupe composé de SEBS, SBS, SBR, EPR, et de caoutchoucs modifiés de ceux-ci.
8. La composition selon la Revendication 4, dans laquelle l'élastomère caoutchouteux en tant que composant (c) est sélectionné parmi le groupe composé de SEBS, SBS, SBR, EPR, et de caoutchoucs modifiés de ceux-ci.
9. La composition selon la Revendication 2, dans laquelle l'élastomère caoutchouteux en tant que composant (d) est sélectionné parmi le groupe composé de SEBS, SBS, SBR et EPR.
10. La composition selon la Revendication 4, dans laquelle l'élastomère caoutchouteux en tant que composant (d) est sélectionné parmi le groupe composé de SEBS, SBS, SBR et EPR.
11. La composition selon la Revendication 3, dans laquelle la matière de charge inorganique en tant que composant (e) est une fibre de verre.
12. La composition selon la Revendication 4, dans laquelle la matière de charge inorganique en tant que composant (e) est une fibre de verre.